Investigation on mechanism of phosphate removal on carbonized sludge adsorbent

Lei Zhang¹,², Junxin Liu¹,²,⁎, Xuesong Guo¹

¹. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
². University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

For the removal of phosphate (PO₄³⁻) from water, an adsorbent was prepared via carbonization of sewage sludge from a wastewater treatment plant: carbonized sludge adsorbent (CSA). The mechanism of phosphate removal was determined after studying the structure and chemical properties of the CSA and its influence on phosphate removal. The results demonstrate that phosphate adsorption by the CSA can be fitted with the pseudo second-order kinetics and Langmuir isotherm models, indicating that the adsorption is single molecular layer adsorption dominated by chemical reaction. The active sites binding phosphate on the surface are composed of mineral particles containing Si/Ca/Al/Fe. The mineral containing Ca, calcite, is the main factor responsible for phosphate removal. The phosphate removal mechanism is a complex process including crystallization via the interaction between Ca²⁺ and PO₄³⁻; formation of precipitates of Ca²⁺, Al³⁺, and PO₄³⁻; and adsorption of PO₄³⁻ on some recalcitrant oxides composed of Si/Al/Fe.

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Introduction

Excess phosphorus is a key factor contributing to the eutrophication of water bodies receiving wastewater treatment effluents (Wang et al., 2016b). On the other hand, phosphorus is a limited resource and gradually declining in other areas (Van Vuuren et al., 2010). Therefore, the recovery of phosphorus from sewage will not only reduce water pollution, but also phosphorus resource shortages. Phosphorus in sewage is generally in the form of phosphate (PO₄³⁻). The amount of phosphate in municipal sewage is close to 5.5% of the amount of phosphorus fertilizer in China (Zhou et al., 2017). The common treatment methods of sewage, such as chemical and biological methods, generally remove phosphate as a pollutant by forming precipitates, but it is very difficult to recover phosphate from the generated sludge (Chen et al., 2016). It may be possible to recover phosphate from wastewater using adsorption and crystallization methods (Cui et al., 2016b; Hermassi et al., 2015). At present, the preparation of adsorbents for phosphate removal from water mainly focuses on natural minerals, industrial wastes, and novel materials prepared via synthesis or modification (Chen et al., 2016; Cui et al., 2016a; Seliem et al., 2016), whereas different types of phosphate adsorbents show remarkable discrepancies regarding efficiency and cost. The key hot spot for adsorption research is to select or prepare adsorbents with low cost and high capacity that are considered environmentally friendly (Bal Krishna et al., 2016), allowing for an economical and simple pathway to achieve phosphorous recovery.

Many studies have shown that adsorbents containing Ca/Mg/Al/Fe oxides exhibit good ability to remove phosphate from sewage (Li et al., 2016b; Nair and Ahammed, 2015). Additionally, some researchers prepared adsorbents by
introducing the elements Zr and La to form oxides to enhance phosphate adsorption (Wang et al., 2016b; Zhang et al., 2012). These adsorbents mainly remove the phosphate in water that exists in several other forms, including H$_3$PO$_4$, H$_2$PO$_4$ or HPO$_4^{2-}$, under different environmental conditions (Seliem et al., 2016). So far, the generally accepted mechanisms of phosphate adsorption mainly include (Chen et al., 2015; Cui et al., 2016a): (I) electrostatic attraction between phosphate ions and the positively charged hydroxylated surface of metal oxides derived from protonation, (II) ligand exchange between H$_2$PO$_4$ or HPO$_4^{2-}$ phosphate and the hydroxyl group ligand on the surface of adsorbents, and (III) formation of water-insoluble precipitates with the metal ions introduced. All of those might occur when adsorbents containing Fe/Al/Mg/Zr/La metal elements are applied. For Ca-rich adsorbent materials, however, phosphate removal is dependent on Ca-P crystal or precipitate applied. For Ca-rich adsorbent materials, however, phosphate removal was also analyzed. It is expected that this work could provide more support for further improving the applicability of this method.

1. Materials and methods

1.1. Experimental materials

1.1.1. Carbonized sludge adsorbent

The adsorbent used in the experiments was prepared from sewage sludge collected from a municipal sewage treatment plant in Beijing, where an A2O process with a sewage capacity of 600,000 tons/day is employed. For pretreatment, the sludge was first dried at 105°C to constant weight in a laboratory oven, then the dry sludge was ground and sieved to a particle size $< 0.15$ mm. The proximate analysis of dried sewage sludge showed that the contents of volatiles, ash, and fixed carbon were 54.35%, 45.08%, and 0.58%, respectively. Elemental analysis was also carried out. To be specific, the weight percentages of C and O were considerably higher than those of other non-metal elements (N, S, Si and P). In addition, the presence of several metallic elements (Ca, Mg, Al, Fe, Na and K) was also revealed, in which Fe and Ca were determined to have the highest contents of up to 7.66% and 4.83%, respectively. In the preparation process, the dry sludge particles were placed in a porcelain crucible with a lid and transferred into a muffle furnace and heated at a heating rate of 23°C/min from ambient temperature to 690°C, and kept at that temperature for 1 hr. After being cooled back down to ambient temperature, the residual was ground to a particle size $< 0.15$ mm and labeled as CSA. In the current study, a majority of carbon black material was observed with a thin ash layer on its surface.

1.1.2. Carbonized sludge adsorbents with surface mineral components depleted

The adsorbent CSA was treated by acid washing to eliminate mineral particles on the surface of the adsorbent. Two methods for acid washing were employed. (1) Adsorbent modification by one-step acid washing (CSA-D-1): The CSA was mixed with 1 mol/L HCl at a ratio of 1 g:10 mL in a beaker, and then placed in a 25°C rotary shaker for 30 min followed by centrifugation and removal of the supernatant. This process was repeated three times. After acid washing, the solid was rinsed with deionized water until the effluent had a neutral pH. Finally, the solid was placed in a 105°C oven for dehydration, resulting in an adsorbent modified by one-step acid washing, designated CSA-D-1. (II) Adsorbent modification by two-step acid washing (CSA-D-2): The CSA-D-1 was mixed with 1 mol/L HCl + HF solution at a ratio of 1 g:10 mL in a beaker. The beaker was placed in a 25°C rotary shaker for 30 min followed by centrifugation and removal of the supernatant. This process was repeated three times. After acid washing, the solid was rinsed with deionized water until the effluent was neutral. After dehydration in a 105°C oven, the resultant solid was designated as an adsorbent modified by two-step acid washing and labeled CSA-D-2.

The stock solution of phosphate, with a concentration of 500 mg/L (calculated as P), was prepared with KH$_2$PO$_4$ and deionized water. Other solutions containing various amounts of phosphate were obtained by diluting the stock solution. The reagents HCl, HF, and NaOH purchased from Sinopharm Chemical Reagent Co., China were all of analytical grade.
1.2. Experimental design

Phosphate removal performance by the CSA was determined via batch experiments. In a 100 mL conical flask, 0.4 g CSA was mixed with 50 mL phosphate solution at various concentrations. The pH in the solution was adjusted to 7. The conical flask was placed in a 25°C rotary shaker for the adsorption process. Then, the mixture was centrifuged and the supernatant was used to determine the residual phosphate.

To determine whether the CSA would release cations to water and the effect of mineral particle dissolution on phosphate removal, the phosphate solution was replaced with deionized water to act as a control. The ion composition and pH value at set time intervals were recorded for the control and experimental samples to calculate the saturation extent in the solution and determine the possibility of the formation of insoluble substances.

1.3. Analysis methods

X-ray diffraction (XRD) patterns were collected by an X-ray diffractometer (X’Pert PRO MPD, PANalytical, Holland) with Cu-Kα radiation in the 2θ range of 3° to 90°, and phase analysis was performed using X’Pert HighScore Plus software. Chemical composition analysis was carried out with a wavelength dispersive X-ray fluorescence spectrometer (XRF, Rigaku, Japan). The morphology and surface element analyses were performed via field emission scanning electron microscopy (FE-SEM) coupled with energy dispersive X-ray spectroscopy (EDS) (SU-8020, Hitachi Co., Japan). The specific surface area and pore size distribution were measured according to nitrogen adsorption isotherms using an automatic micropore and mesopore analyzer (ASAP 2020HD88, USA), with the two characteristics calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods (Wang et al., 2016a), respectively. The binding state and formation of PO₄³⁻ on the CSA were identified using X-ray photoelectron spectroscopy (AXIS Ultra, Shimadzu, Japan). The phosphate concentration was determined by a UV–vis spectrophotometer (UV-1700, Hitachi Co., Japan) on the basis of the molybdenum blue method of the National Standard of China (GB/T 6913-2008).

1.4. Calculation methods

The removal efficiency and adsorption capacity of PO₄³⁻ were calculated as follows:

\[ \eta = \frac{(C_0 - C_t)}{C_0} \times 100\% \]  \hspace{1cm} (1)\n
\[ q = \frac{(C_0 - C_t)V}{m} \]  \hspace{1cm} (2)\n
where \( \eta \) (%) is the removal efficiency; \( q \) (mg/g) is the adsorption capacity; \( C_0 \) (mg/L) and \( C_t \) (mg/L) are the initial and final concentrations of PO₄³⁻, respectively; \( V \) (mL) is the phosphate solution volume; and \( m \) (g) is the amount of adsorbent. In this work, all the phosphate concentrations were calculated based on the P in PO₄³⁻.

The saturation index is an index used to simulate and predict the solution stability and possibility of insoluble matter generation in aqueous solution, shown in the following equation.

\[ \text{Sat.index} = \log \text{IAP} - \log K_s \]  \hspace{1cm} (3)\n
where Sat.index is the calculated saturation index, IAP is the actual ionic activity product, and \( K_s \) is the solubility product constant dependent on temperature. Sat.index analyses were conducted using Visual MINTEQ 3.1 (Li et al., 2016a). The software Visual MINTEQ was compiled by Prof. Jon Petter Gustafsson from the Royal Swedish Institute of Technology based on a US Environmental Protection Agency database. Identification was carried out according to the fact that a
material or precipitate would be generated, and greater values imply more possibility of precipitation if Sat.index > 0. On the contrary, the solution is not at saturation state with a precipitate not appearing if Sat.index < 0.

Adsorption kinetic features were described by the pseudo-first-order model and the pseudo-second-order model (Huang et al., 2015), with the linear equations shown as follows:

\[
\ln \left( \frac{q_e - q_t}{q_e} \right) = -K_1 t
\]

\[
\frac{t}{q_t} = \frac{1}{K_2 q_t^2} + \frac{1}{q_m}
\]

where \( q_e \) (mg/g) is the adsorption capacity at equilibrium; \( q_t \) (mg/g) is the capacity at time \( t \) (hr) is the reaction time; and \( k_1 \) (g/(mg·hr)) and \( k_2 \) (g/(mg·hr)) are the rate constants of the pseudo-first-order and the pseudo-second-order models, respectively.

Adsorption isothermal properties were fitted by the Langmuir, Freundlich, and Temkin models, with their respective linear forms expressed in Eqs. (6)–(8) (Yang et al., 2014):

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}
\]

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

\[
q_e = B \ln K_T + B \ln C_e
\]

where \( C_e \) (mg/L) is the equilibrium concentration of phosphate; \( q_e \) (mg/g) is the adsorption capacity at equilibrium; \( K_L \) (l/mg) is the Langmuir equilibrium constant; \( q_m \) (mg/g) is the maximum adsorption capacity computed by the Langmuir model, \( K_F \) (l/mg) and \( \frac{1}{n} \) (dimensionless) are Freundlich constants; \( K_T \) (l/mg) is the binding constant related to maximum binding energy; and \( B \) represents the heat of adsorption, which can be calculated by the definition \( B = RTb \) for which \( R \) (8.314 J/(mol·K)) is the universal gas constant, \( T \) (K) is the absolute temperature, and \( b \) reflects the adsorption potential.

2. Results and discussion

2.1. Characterization of adsorbents

CSA, CSA-D-1, and CSA-D-2 were characterized based on morphology and porosity, with the results shown in Fig. 1 and Table 1, respectively. It was observed that a few mineral
particles in CSA were depleted, and more porosity appeared on the surfaces of the CSA-D-1 and CSA-D-2 samples than on that of CSA. The order of specific surface area ($S_{BET}$), average pore size ($D_p$), and pore volume ($V_{total}$), from lowest to highest, was CSA < CSA-D-1 < CSA-D-2. Impurities on the CSA were eliminated with acid washing, and the two-step acid washing was superior to the one-step acid washing in that regard.

The results of EDS analysis for the whole surface area of adsorbents are shown as Fig. 2, with the percentage of each element presented in Table 2. The contents of Ca, Mg, Al, Fe, and other elements, excluding C and S, on the surface were significantly reduced when the acid washing process was increased, and Si could be depleted by HF during the process of two-step acid washing. The complete chemical compositions of the CSA, CSA-D-1, CSA and CSA-D-2 were determined using XRF (Table 3). The nonmetallic (O and Si) and metallic (Ca, Mg, Al, Fe, Na, and K) elements remarkably declined with the increase in the extent of stripping from the one-step acid washing to the two-step acid washing. On the contrary, the ratios of C, N, and S increased, indicating that the acid washing mainly removes the Si and metal oxide components in the adsorbent, leading to more of the carbon matrix being exposed.

The XRD patterns are presented in Fig. 3. According to PDF2004 standard cards, the peaks at $2\theta = 20.848^\circ$, $50.125^\circ$, and $54.855^\circ$ were ascribed to quartz (SiO$_2$, JCPDS no. 86-1560). The peaks at $2\theta = 26.543^\circ$, $42.321^\circ$, and $59.852^\circ$ indicate the existence of graphite, C: Carbon, O: Quartz, SiO$_2$: Calcite, CaCO$_3$: Hematite, $\alpha$-Fe$_2$O$_3$: Aluminum Oxide, Al$_2$O$_3$: Brucite, Mg(OH)$_2$.

---

**Fig. 3** – X-ray diffraction (XRD) analysis of three adsorbents CSA, CSA-D-1 and CSA-D-2. ★ Graphite, C ● Carbon, C ◆ Quartz, SiO$_2$ ▲ Calcite, CaCO$_3$ #: Hematite, $\alpha$-Fe$_2$O$_3$ ◇ Aluminum Oxide, Al$_2$O$_3$ &: Brucite, Mg(OH)$_2$.

**Fig. 4** – Adsorption capacities of three adsorbents CSA, CSA-D-1 and CSA-D-2 with initial PO$_4^{3-}$ concentration at 35 mg/L.

**Fig. 5** – The influence of reaction time on phosphate adsorption by CSA.
of graphite (C, JCPDS no. 65-6212). Both graphite and quartz were identified in the three adsorbents, with intensities from lowest to highest following the order CSA < CSA-D-1 < CSA-D-2. Calcite (CaCO$_3$, JCPDS no. 83-0578) was found in CSA based on the peaks at 29.410° and 31.451°, whereas it was not present in CSA-D-1 and CSA-D-2. This indicated that the acid washing depleted mineral particles such as calcite, resulting in an increase in the ratio of C, thus exposing more of the carbon matrix.

2.2. Phosphate removal by carbonized sludge adsorbents

The phosphate adsorption capacities of CSA, CSA-D-1, and CSA-D-2 in a 35 mg/L phosphate solution with initial pH adjusted to 7 are represented in Fig. 4. The adsorption capacities were found to be 2.99, 1.48, and 1.05 mg/g for CSA, CSA-D-1, and CSA-D-2. In comparison with the original adsorbent CSA, the adsorption capacities of CSA-D-1 and CSA-D-2 were lower by 51% and 65%, respectively. Coupled with the structural data shown in Table 1, the phosphate removal for CSA-D-1 and CSA-D-2 would be impaired even though the structural porosities were more developed than that of CSA. The results demonstrated that the developed porosity is not the dominant factor affecting phosphate removal.

The influence of time on adsorption by the CSA was studied using three phosphate solutions with the concentrations of PO$_4^{3-}$ set at 25, 30, and 35 mg/L. As shown in Fig. 5, the phosphate adsorption capacity increased with reaction time, showing a surge in the first 10 hr. After 15 hr, the phosphate

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Ca$_{10}$(PO$_4$)$_6$(OH)$_2$</th>
<th>Ca$_3$(PO$_4$)$_2$</th>
<th>Al(OH)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.859</td>
<td>3.549</td>
<td>-9.197</td>
</tr>
<tr>
<td>0.25</td>
<td>12.987</td>
<td>3.596</td>
<td>-9.236</td>
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<td>0.5</td>
<td>12.664</td>
<td>2.91</td>
<td>-8.959</td>
</tr>
<tr>
<td>1</td>
<td>12.460</td>
<td>3.124</td>
<td>-9.146</td>
</tr>
<tr>
<td>3</td>
<td>12.239</td>
<td>3.087</td>
<td>-9.324</td>
</tr>
<tr>
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<td>12.549</td>
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<td>-9.643</td>
</tr>
<tr>
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<td>12.478</td>
<td>3.037</td>
<td>-9.732</td>
</tr>
<tr>
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<td>3.12</td>
<td>-9.622</td>
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<tr>
<td>18</td>
<td>12.393</td>
<td>2.99</td>
<td>-9.601</td>
</tr>
<tr>
<td>24</td>
<td>12.536</td>
<td>3.071</td>
<td>-9.703</td>
</tr>
</tbody>
</table>

Fig. 6 – The comparison of material in the adsorption experiment with PO$_4^{3-}$ and control trial.

Fig. 7 – X-ray diffraction (XRD) analysis of CSA after phosphate adsorption.
adsorption was at equilibrium, and the capacity increased as the phosphate concentration increased.

To study whether the mineral particles in the CSA would be dissociated and contribute to PO$_4^{3-}$ removal by affecting the form of Ca$^{2+}$, the concentrations of other components (such as Ca$^{2+}$ and Al$^{3+}$) and pH values were measured in the phosphate (35 mg/L PO$_4^{3-}$) and control (deionized water) solutions. As shown in Fig. 6, Ca$^{2+}$ and Al$^{3+}$ ions were detected in the deionized water, and it was obvious that the concentration of Ca$^{2+}$ (with maximum value over 40 mg/L) was much higher than Al$^{3+}$ (with maximum concentration below 2 mg/L). When adding CSA into phosphate solution, the concentration of Ca$^{2+}$ was found to decrease remarkably, with a maximum decrease of 30 Pseudo.

The index Sat.index was calculated using Visual MINTEQ 3.1 software, the results of which are shown in Table 4. Based on the results, some solid materials would be formed including hydroxyapatite Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ and Whitlockite Ca$_3$(PO$_4$)$_2$, and the Sat.index of Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ was higher than that of Ca$_3$(PO$_4$)$_2$, implying PO$_4^{3-}$ would mainly be removed by forming Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ with the ions Ca$^{2+}$ and OH$^{-}$. The XRD characterization of CSA after the adsorption of phosphate is shown in Fig. 7. In comparison to the initial adsorbent (shown in Fig. 3), the characteristic peaks for newly formed minerals, such as Hydroxylapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$), Whitlockite (Ca$_3$(PO$_4$)$_2$) and Monetite (CaHPO$_4$), were identified according to JCPDS no. 84-1998, JCPDS no. 09-0169 and JCPDS no. 71-1759, respectively. This observation is consistent with the results predicted by Visual MINTEQ 3.1. The Sat. index for Al(OH)$_3$ was negative, indicating that Al$^{3+}$ could not stably exist in the PO$_4^{3-}$ solution and might tend to precipitate with PO$_4^{3-}$.

2.3. Phosphate removal mechanism of carbonized sludge adsorbent CSA

The kinetics experimental data for the CSA in Fig. 5 were fitted by the pseudo first-order and pseudo second-order models, with the parameters shown in Table 5. The pseudo second-order model was better at fitting the adsorption data than the pseudo first-order model, with all $R^2 > 0.99$ for various phosphate

| Table 5 – The kinetics parameters of phosphate adsorption on CSA. |
|-----------------|-----------------|--------|--------|
| Concentration (mg/L) | Model | Parameters | Values | $R^2$  |
|                  |       |           |       |       |
| 25               | Pseudo | $K_t$ | 0.2235 | 0.915 |
|                  | first-order | $q_e$ | 1.53  |  |
|                  | Pseudo | $K_t$ | 0.3818 | 0.9974 |
|                  | second-order | $q_e$ | 2.7108 |  |
|                  | Pseudo | $K_t$ | 0.2599 | 0.9437 |
|                  | first-order | $q_e$ | 2.62  |  |
|                  | Pseudo | $K_t$ | 0.2558 | 0.9961 |
|                  | second-order | $q_e$ | 3.0358 |  |
|                  | Pseudo | $K_t$ | 0.2734 | 0.9192 |
|                  | first-order | $q_e$ | 3.35  |  |
|                  | Pseudo | $K_t$ | 0.1913 | 0.9925 |
|                  | second-order | $q_e$ | 3.2595 |  |

Table 6 – Adsorption isotherm parameters for phosphate adsorption on CSA.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Model</th>
<th>Parameters</th>
<th>Values</th>
<th>$R^2$</th>
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<tr>
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<td>$q_m$</td>
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<td></td>
</tr>
<tr>
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<td>Temkin</td>
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<td>0.937</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
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<td>$b$</td>
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<tr>
<td>45</td>
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<td>$b$</td>
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Fig. 8 – Adsorption isotherms of PO$_4^{3-}$ on CSA.

This implied that phosphate adsorption on the CSA was dependent on chemical adsorption, not on physical adsorption (Yoon et al., 2014).

The adsorption isotherms for the CSA at various temperatures are shown in Fig. 8. The adsorption capacity at equilibrium increased with the increase of the equilibrium concentration of PO$_4^{3-}$. When the PO$_4^{3-}$ concentration increased to a certain extent, the equilibrium adsorption capacity increased more slowly up to the maximum. Temperature increase from 30 to 55°C improved the maximum adsorption capacity, indicating that the adsorption was endothermic. The isotherm fitting results are listed in Table 6. It was observed that the $R^2$ at three different temperatures were uniformly above amounts. This implied that phosphate adsorption on the CSA was dependent on chemical adsorption, not on physical adsorption (Yoon et al., 2014).
0.999, which demonstrated that PO$_4^{3-}$ was adsorbed in the form of monomolecular layers (Seliem et al., 2016). Additionally, the fitting results of the Temkin model were superior to those of the Freundlich model at temperatures from 30 to 55°C, which means that chemical reaction is the main driving force for PO$_4^{3-}$ removal.

The binding forms of PO$_4^{3-}$ on CSA were analyzed by XPS (shown in Fig. 9 and Table 7). The binding energies of Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, Ca$_3$(PO$_4$)$_2$ and CaHPO$_4$ are at 133.2 eV (Tanizawa et al., 1991), 133.8 eV (Demri and Muster, 1995) and 133.6 eV (Barbaux et al., 1992), respectively. Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ and Ca$_3$(PO$_4$)$_2$ were the primary compounds deposited onto CSA. With further removal of phosphate, the ratio of Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ (shown in Table 7) increased from 82.6% to 87.7%. On the contrary, the ratio of Ca$_3$(PO$_4$)$_2$ decreased from 17.4% to 12.3%. CaHPO$_4$ was neglected due to its extremely low content (<0.01%). Therefore, it can be deduced that the formation of Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ via the reaction of Ca$^{2+}$, PO$_4^{3-}$ and OH$^{-}$ is the primary mechanism for the removal of phosphate (Dai et al., 2016). This conclusion is also in accordance with the results predicted by Visual MINTEQ 3.1 and confirmed by XRD analysis (Fig. 7).

Based on the above-mentioned results, PO$_4^{3-}$ removal by the CSA did not take place merely by one single reaction, but rather a series of interactions with active sites on the CSA surface, which is composed of mineral particles containing Ca, Al, Fe, Si, and so on. A complex process including crystallization, precipitation, and adsorption removed the phosphate. This is explained as follows.

1. Synthesis mechanism of Ca-P compounds: Based on the principle of calcite (CaCO$_3$) hydrolysis, the resulting Ca$^{2+}$ can combine with PO$_4^{3-}$, HPO$_4^{2-}$, and OH$^{-}$ to form crystal particles or precipitate (Liu et al., 2012; Oladoja et al., 2012). The formation of a Ca-P compound can lead to PO$_4^{3-}$ removal from water while the mineral particles of CaCO$_3$ and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ would provide a layer rich in Ca for subsequent attachment of the generated Ca$_{10}$(PO$_4$)$_6$(OH)$_2$. Meanwhile, the PO$_4^{3-}$ in solution could be combined with the Ca$^{2+}$ and converted to Ca$_3$(PO$_4$)$_2$.

2. Synthesis mechanism of Al-P compound: Some Al species present as Al$^{3+}$ or Al$_2$O$_3$ (Tables 3, 4, Figs. 3, and 6) in the CSA would be hydrolyzed into Al$^{3+}$, then the formation of AlPO$_4$ from Al$^{3+}$ and PO$_4^{3-}$ was responsible for part of the phosphate removal (Georgantas and Grigoropoulou, 2007).

3. Adsorption of PO$_4^{3-}$ by active sites on the surface of the CSA: As seen from the results presented in Table 3, Figs. 2, and 4, the proportions of nonmetallic (O and Si) and metallic (Ca, Mg, Al, Fe, Na, and K) elements were remarkably depleted, but the phosphate removal by CSA-D-1 and CSA-D-2 did not disappear completely. That is because a small portion of mineral particles, such as Fe$_2$O$_3$, Al$_2$O$_3$, and SiO$_2$, were resistant to depletion by acid washing. Ligand hydroxyl groups on the hydrous oxide surface of those particles are generated in aqueous solution, which could bind other types of PO$_4^{3-}$ such as HPO$_4^{2-}$ and H$_2$PO$_4^{-}$ through ligand exchange (Xue et al., 2009; Yan et al., 2014). In the experiments, the pH in solution after phosphate removal by CSA-D-1 and CSA-D-2 showed a slight increase, indicating that ligand exchange between phosphate and ligand hydroxyl groups took place.

### Table 7 – The binding of PO$_4^{3-}$ phases on CSA and the relative content.

<table>
<thead>
<tr>
<th>Item</th>
<th>Binding energy (eV)</th>
<th>Before adsorption (%)</th>
<th>After adsorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>133.2</td>
<td>82.6</td>
<td>87.7</td>
</tr>
<tr>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>133.8</td>
<td>17.4</td>
<td>12.3</td>
</tr>
<tr>
<td>CaHPO$_4$</td>
<td>133.6</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

3. Conclusions

CSA prepared from sewage sludge can effectively remove phosphate from water. Phosphate adsorption can be well fitted by the pseudo-second-order kinetics and Langmuir isotherm models. It is deduced that the phosphate adsorption on CSAs is a process dominated by chemical reactions leading to single-molecular layer adsorption.
CSA is composed of a carbon matrix and mineral particles containing Si, Ca, Al, and Fe on the surface. The mineral particles serve as the active sites binding phosphate. A decline in the mineral amount will lead to a decrease in phosphate removal.

Phosphate removal by CSA is dominated by a complex process including crystallization and precipitation via calcite, precipitation via $\text{Al}^{3+}$, and ligand exchange derived from oxides containing Si, Al, and Fe to some extent. Among all the mechanisms, the contribution from calcite is the most significant.

Acknowledgments

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References


